Frost, Ray and Cejka, Jiri and Ayoko, Godwin and Dickfos, Marilla (2007) Raman spectroscopic study of the multi-anion uranyl mineral schroeckingerite. *Journal of Raman Spectroscopy* 38:pp. 1609-1614.

Raman spectroscopic study of the multi-anion uranyl mineral schroeckingerite

Ray L. Frost [1•] , Jiří Čejka [1,2] , Godwin A. Ayoko [1] and Marilla J. Dickfos [1]

Inorganic Materials Research Program, School of Physical and Chemical Sciences, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[2] National Museum, Václavské náměstí 68, CZ-115 79 Praha 1, Czech Republic.

Abstract

Raman spectroscopy complimented with infrared spectroscopy has been used to study the mineral schroeckingerite. The mineral is a multi-anion mineral and has $(UO_2)^{2+}$, $(SO_4)^{2-}$, and $(CO_3)^{2-}$ units in its structure and bands attributed to these vibrating units are readily identified in the Raman spectra. Symmetric stretching modes at 815, 983 and 1092 cm^{-1} are assigned to $(UO_2)^{2+}$, $(SO_4)^{2-}$, and $(CO_3)^{2-}$ units, respectively. The antisymmetric stretching modes of $(UO_2)^{2+}$, $(SO_4)^{2-}$ are not observed in the Raman spectra but may be readily observed in the infrared spectrum at 898 and 1180 cm^{-1}. The antisymmetric stretching mode of $(CO_3)^{2-}$ is observed in the Raman spectrum at 1374 cm^{-1} as is also the ν_4 $(CO_3)^{2-}$ bending modes at 742 and 707 cm^{-1}. No ν_2 $(CO_3)^{2-}$ bending modes are observed in the Raman spectrum of schroeckingerite. All the spectroscopic evidence points to a highly ordered structure of this mineral.

Keywords: uranyl sulphate, uranyl carbonate, fluoride, infrared and Raman spectroscopy

Introduction

The study of the uranyl carbonates has been undertaken for an extended period of time. [1,2]There are a significant number of compounds containing the uranyl ion [3]. Included in these are many uranyl carbonates. [4-6] These uranyl carbonates may be divided into those based upon tricarbonates and those with single carbonate in the formula such as rutherfordine (UO_2CO_3) [7-9] and blatonite ($UO_2CO_3.H_2O$). [10] Sharpite is a basic uranyl carbonate $Ca(UO_2)_6(CO_3)_5(OH)_4.6H_2O$ [11,12]. Many of these minerals have been synthesised. [13,14] Among the tricarbonates minerals is the mineral andersonite $Na_2Ca(UO_2)_6(CO_3)_3.xH_2O$ [15-17] where x is variable but may be a number between 5 and 6. Many of these minerals may be readily synthesised and there chemistry studied by the normal analytical techniques. [18,19] Uranyl anion sheet topology has been discussed by Burns in some detail. [20,21] Some papers on uranyl carbonates [22-25]and sulphates [26-29] have been published by the authors. Other carbonates are more complex with more than one anion in the structure. The mineral schroeckingerite is a multi-anion mineral and has $(UO_2)^{2+}$, $(SO_4)^{2-}$, and $(CO_3)^{2-}$ units in its structure

• Author for correspondence Ray L. Frost (r.frost@qut.edu.au)

Among these analytical techniques is infrared and Raman spectroscopy. These techniques serve to find information about the molecular structure of minerals which is not obtained through X-ray diffraction techniques such as single crystal or powder X-ray diffraction. In particular information on the structure of hydroxyl groups may be obtained. Further vibrational spectroscopy determines parameters at the chemical bond level as opposed to the lattice. Often infrared spectroscopy has been applied to the study of the uranyl carbonates [2,15,16,19,30] and yet very little work based upon Raman spectroscopy has been forthcoming.

The uranyl mineral schroeckingerite $NaCa_3(UO_2)(CO_3)_3(SO_4)F.10H_2O$ is a multi-anion uranyl mineral containing the uranyl tricarbonate anion. [2,31-33] The mineral is probably an uncommon alteration product of uraninite in the oxidised zone of uranium deposits and is probably of post mining origin. Frondel published some information in a US geological report. [34] Infrared spectra of schroeckingerite has been published [35] and Urbanec and Cejka made some tentative interpretation of the infrared spectrum. [5] No vibrational spectroscopic analysis of this mineral has been published. The mineral is triclinic with space group P 1(-). [36] The unit cell parameters are a = 9.6340 | b = 9.6350 | c = 14.3910 | alpha = 91.4100 | beta = 92.3300 | gamma = 120.2600. There are two formula units in the unit cell. [36] Schroeckingerite is a structurally and chemically complex mineral. [20,21,36] The $(UO_2)(CO_3)_3$, a NaO_6 octahedron, a SO_4 tetrahedron and three symmetrically distinct CaO_6 polyhedra link to form sheets with water molecules located in the interlayer between the sheets where they are held by hydrogen bonds only. [21,36]

Raman spectroscopy has proven very useful for the study of minerals. [22,37-51] Indeed Raman spectroscopy has proven most useful for the study of diagentically related minerals as often occurs with carbonate minerals. [22,43,44,46-48,52] Some previous studies have been undertaken by the authors using Raman spectroscopy to study complex secondary minerals formed by crystallisation from concentrated sulphate solutions. [53] No detailed spectroscopic studies of the uranyl mineral schroeckingerite has been forthcoming Few Raman studies of any note are available. [54,55] The aim of this paper is to present Raman and infrared spectra of schroeckingerite. The paper is a part of systematic studies of vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs.

Experimental

Minerals

The schroeckingerite mineral was obtained from the Mineralogical Research Company and originated from Wamsutter, Sweetwater County, Wyoming, USA. The samples were phase analysed by X-ray diffraction and for chemical composition by EDX measurements. The chemical composition of this mineral has been published (page 624). [56] The mineral corresponds to the formula above $NaCa_3(UO_2)(CO_3)_3(SO_4)F.10H_2O$.

Raman microprobe spectroscopy

The crystals of schroeckingerite were placed and oriented on the stage of an Olympus BHSM microscope, equipped with 10x and 50x objectives and part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a HeNe laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Repeated acquisition using the highest magnification was accumulated to improve the signal to noise ratio. Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Details of the technique have been published by the authors [22,23,28,57].

Mid-IR spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio.

Spectral manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentz-Gauss cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

Spectroscopy of uranyl cation

The $D_{\infty h}$ symmetry of the free uranyl, $(UO_2)^{2+}$, Td symmetry of the $(SO_4)^{2-}$ groups, and D_{3h} symmetry of the $(CO_3)^{2-}$ groups lowering may cause infrared and Raman activation of all $(UO_2)^{2+}$, $(SO_4)^{2-}$, and $(CO_3)^{2-}$ vibrations and splitting of doubly and triply degenerate vibrations in the spectra of schroeckingerite. In the crystal structure of schroeckingerite, there are three symmetrically distinct $(CO_3)^{2-}$, one symmetrically distinct $(SO_4)^{2-}$ and $(UO_2)^{2-}$ groups, and symmetrically distinct water molecules. Characteristic vibrations of the uranyl, $(UO_2)^{2+}$, ion: the ν_1 symmetric stretch (approximately 900-750 cm^{-1}), ν_3 antisymmetric stretch (approximately 1000-850 cm^{-1}), and ν_2 (δ) doubly degenerate bend (approximately 300-200 cm^{-1}) may be observed in the studied Raman and infrared spectra The tentative assignment of the observed bands is therefore made with regard to these assumptions.

Spectroscopy of carbonate anion

The free ion, CO_3^{2-} with D_{3h} symmetry exhibits four normal vibrational modes; a symmetric stretching vibration (ν_1), an out-of-plane bend (ν_2), a doubly degenerate antisymmetric stretch (ν_3) and another doubly degenerate bending mode (ν_4). The symmetries of these modes are A_1' (R) + A_2'' (IR) + E′ (R, IR) + E′′ (R, IR) and occur at 1063, 879, 1415 and 680 cm^{-1} respectively. Generally, strong Raman modes appear around 1100 cm^{-1} due to the symmetric stretching vibration (ν_1), of the carbonate groups, while intense IR and weak Raman peaks near 1400 cm^{-1} are due to the antisymmetric stretch (ν_3). Infrared modes near 800 cm^{-1} are derived from the out-of-plane bend (ν_2). Infrared and Raman modes around 700 cm^{-1} region are due to the in-plane bending mode (ν_4). This mode is doubly degenerate for undistorted CO_3^{2-} groups. As the carbonate groups become distorted from regular planar symmetry, this mode splits into two components. Infrared and Raman spectroscopy provide sensitive test for structural distortion of CO_3^{2-}.

Spectroscopy of sulphate anion

In aqueous systems, the sulphate anion is of T_d symmetry and has symmetric stretching mode (ν_1) at 981 cm^{-1}, the antisymmetric stretching mode (ν_3) at 1104 cm^{-1}, the symmetric bending mode (ν_2) at 451 cm^{-1} and the ν_4 mode at 613 cm^{-1} [58,59]. For example, Raman spectrum of the mineral chalcanthite shows a single symmetric stretching mode at 984.7 cm^{-1}. Two ν_2 modes are observed at 463 and 445 cm^{-1} and three ν_3 modes at 1173, 1146 and 1100 cm^{-1}. The ν_4 mode is observed as a single band at 610 cm^{-1}.

The infrared spectroscopy of uranyl sulphate compounds has been undertaken. [31] Raman spectroscopy has also been recently used to understand the chemistry of uranyl sulphates. [28] The spectroscopy has been based on treating the components of uranopilite as separate vibrating entities. [60,61] Thus the infrared spectra are assigned to $(UO_2)^{2+}$, $(SO_4)^{2-}$, $(OH)^-$ and H_2O units. Whether such as assumption is valid is questionable. One of the difficulties of studying the uranyl minerals is the potential overlap of bands from these different units. Both the ν_1 and ν_3 SO_4 stretching modes may overlap with UOH deformation modes. Čejka et al. have shown that a band at 930 cm^{-1} is assignable to the antisymmetric stretching modes of the $(UO_2)^{2+}$ units. The band appears to be very variable in position for zippeites [62]. Bands were identified at between 880 and 924 cm^{-1}. The intensity of the ν_1 symmetric stretching vibration was very weak in the infrared spectrum of uranopilite and the band at 840 cm^{-1} was assigned to this vibration.

Raman Spectroscopy

The Raman spectrum of schroeckingerite in the 100 to 1500 cm^{-1} region is shown in Figure 1. Distinct sharp bands are observed which may be readily attributed to the various vibrating units of the mineral. The intense sharp band at 815 cm^{-1} is assigned to the ν_1 $(UO_2)^{2+}$ symmetric stretching vibration. In the infrared spectrum of schroeckingerite a low intensity band is observed at 817 cm^{-1} (Figure 2). Urbanec and Cejka published a spectrum of schroeckingerite and interpreted the infrared spectrum of schroeckingerite in 1979. [5] Cejka published the infrared spectrum of schroeckingerite with a comparison with other uranyl carbonates in Reviews in Mineralogy Volume 38. [63] No band positions were provided and no assignment of the bands was forthcoming. A weak infrared band at 816 cm^{-1} was found [63]. A weak

infrared band is observed at 898 cm^{-1} which is not observed in the Raman spectrum of schroeckingerite is assigned to the ν_3 $(UO_2)^{2+}$ antisymmetric stretching vibration. In the infrared spectrum of schroeckingerite as published by Cejka two bands were observed at 903 and 932 cm^{-1}. Jones and Jackson [1993] observed corresponding bands at 822 and 906 cm^{-1} [35]. Wavenumbers of the ν_1 $(UO_2)^{2+}$ vibration (817 cm^{-1}) and ν_3 $(UO_2)^{2+}$ vibration (898 cm^{-1}) were used for the calculation of the U-O bond length in uranyl with two empirical relations by Bartlett and Cooney [64] Obtained values 1.794 and 1.786 Å , respectively, are in agreement with average value 1.788 Å inferred from the X-ray single crystal analysis. [36]

The Raman band at 983 cm^{-1} is attributed to the ν_1 $(SO_4)^{2-}$ symmetric stretching vibration. In the infrared spectrum of schroeckingerite the band at 1180 cm^{-1} is attributed to the ν3 $(SO_4)^{2-}$ antisymmetric stretching vibration. The Raman spectrum of johannite shows an intense sharp intense band at 1042 cm^{-1} attributed to the $(SO_4)^{2-}$ symmetric stretching vibration. Three Raman bands are observed at 1147, 1100 and 1090 cm^{-1} and are assigned to the $(SO_4)^{2-}$ antisymmetric stretching vibrations. The Raman band at 1092 cm^{-1} is assigned to the ν_1 $(CO_3)^{2-}$ symmetric stretching vibration. In the infrared spectrum of schroeckingerite two overlapping bands at 1077 and 1097 cm^{-1} are found. Cejka determined bands at 1078 (weak) and 1093 cm^{-1} (strong). [63] One probable assignment is that these bands are assignable to the infrared activated ν_1 $(CO_3)^{2-}$ symmetric stretching vibration. In andersonite there are two structurally distinct $(CO_3)^{2-}$ units and as a consequence two symmetric stretching modes two well resolved bands at 1092 and 1080 cm^{-1} are observed. The band at 1374 cm^{-1} is assigned to the ν_1 $(CO_3)^{2-}$ antisymmetric stretching vibration. In schroeckingerite, there are three structurally distinct $(CO_3)^{2-}$ units and as a consequence more symmetric stretching modes and therefore more overlapped bands at 1097 and 1077 cm^{-1} are observed. The infrared bands at 1365, 1543 and 1574 cm^{-1} are assigned to the ν_3 $(CO_3)^{2-}$ antisymmetric stretching vibration and that at 1180 cm^{-1} to the ν_3 $(SO_4)^{2-}$ antisymmetric stretching band. Urbanec and Čejka [5] observed these bands at 1367, 1572 and 1182 cm^{-1}, respectively, Jones and Jackson [1993] at 1550, 1577 and 1370 cm^{-1} respectively [35].

Two Raman bands are observed at 707 and 742 cm^{-1} may be assigned to the $(CO_3)^{2-}$ ν4 in phase bending modes. Two infrared bands are observed at 705 and 739 cm^{-1} which are also assigned to this vibrational mode. Infrared bands were reported by Cejka at exactly these positions [63] and by Jones and Jackson [1993] at 706 and 741 cm^{-1} . [35] The 739 cm^{-1} infrared band was described as of medium intensity and the 705 cm^{-1} band as medium-weak. The ν_2 bending mode for carbonates varies from around 890 cm^{-1} to 850 cm^{-1}. For smithsonite Farmer reported an infrared band at 870 cm^{-1}.[65] For hydrozincite the infrared band was observed at 837 cm^{-1} [65]. In this work no Raman bands are observed for schroeckingerite in this position. In the infrared spectrum two bands are observed at 817 and 842 cm^{-1} which may be ascribed to the $(CO_3)^{2-}$ ν2 bending mode. Two bands are observed in the Raman spectrum of johannite at 481 and 384 cm^{-1}. These bands are assigned to the ν_2 bending modes of the $(SO_4)^{2-}$ units. Čejka found bands at 422 and 384 cm^{-1} in the infrared absorption spectra of johannite. [66] The Raman band at 471 cm^{-1} for schroeckingerite is assigned to the ν_2 $(SO_4)^{2-}$ bending mode.

In the Raman spectrum two bands are observed at 308 and 157 cm^{-1}. In the infrared spectrum of johannite Čejka assigned the two bands at 257 and 216 cm^{-1} to the doubly degenerate ν_2 bending vibration of the $(UO_2)^{2+}$ units. The two Raman bands at 308 and 157 cm^{-1} fits reasonably well with this observation. However there are significant differences between the infrared spectrum in the low wavenumber region as published by Čejka and the Raman spectrum in this work. There is an intense additional band at 308 cm^{-1} in the 298 K spectrum. It is proposed that this band is a CaO stretching vibration.

In the Raman spectrum of schroeckingerite in the 2500 to 3900 cm^{-1} region, two bands are observed at 3256 and 3432 cm^{-1}(Figure 3) In the infrared spectrum three bands are resolved at 3252, 3414 and 3481 cm^{-1} (Figure 4). The bands are attributed to the stretching modes of water in the schroeckingerite structure. In the spectrum reported by Cejka, a strong band was observed at 3455 cm^{-1} with shoulders at 3260 and 3620 cm^{-1} [63] and Jones and Jackson [1993] bands or shoulders at 3272, 3468 and 3598 cm^{-1}. [35] The bands at 3455 and 3260 correspond reasonably well with the infrared bands observed in this work. In the spectrum in Figure 4, a low intensity band is observed at 3630 cm^{-1} which corresponds to the 3620 cm^{-1} reported by Cejka. A hydrogen bonding network may be inferred in the crystal structure of schroeckingerite from its Raman and infrared spectra, O-H…O bond lengths ~2.73 -> 3.2 Å. [67] This is in agreement with the conclusions from the X-ray single crystal analysis of schroeckingerite.

Conclusions

The uranyl secondary mineral schroeckingerite is an interesting mineral in that it contains three anions namely sulphate, carbonate and fluoride. The cations in the in this mineral are Na, Ca and $(UO_2)^{2+}$ in the form of a uranyl tricarbonate $[(UO_2)(CO_3)_3]$ cluster. Bands which can be attributed to the vibrating units $(UO_2)^{2+}$, $(SO_4)^{2-}$, and $(CO_3)^{2-}$ are readily identified in the Raman spectra through the observation of symmetric stretching modes at 815, 983 and 1092 cm^{-1} respectively. The antisymmetric stretching modes of $(UO_2)^{2+}$, $(SO_4)^{2-}$ are not observed in the Raman spectra but may be readily observed in the infrared spectrum through the observation of bands at 898 and 1180 cm^{-1} respectively. The antisymmetric stretching mode of $(CO_3)^{2-}$ is observed in the Raman spectrum at 1374 cm^{-1} as is also the ν_4 $(CO_3)^{2-}$ bending modes at 742 and 707 cm^{-1}. No ν_2 $(CO_3)^{2-}$ bending modes are observed in the Raman spectrum of schroeckingerite. All this spectroscopic evidence points to a highly ordered structure of this mineral.

Acknowledgments

The financial and infra-structure support of the Queensland University of Technology, Inorganic Materials Research Program is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation.

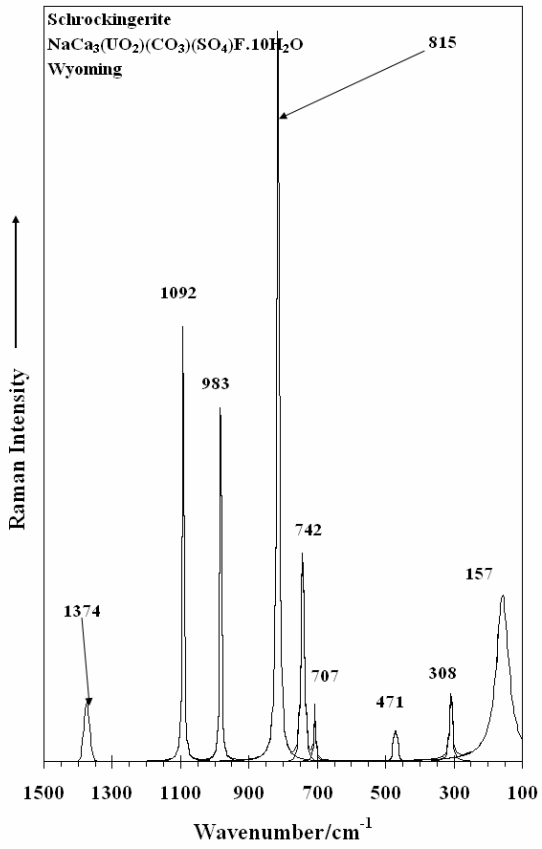
References

1. Neumann, H, Bryn, KO. *Avhandl. Norske Videnskaps-Akad. Oslo., I., Mat.-Naturv. Kl.* 1958: 6 pp.
2. Huang, CK, Kerr, PF. *American Mineralogist* 1960**; 45**: 311.
3. Whittle, AWG. *J. Geol. Soc. Australia* 1955**; 2**: 21.
4. Urbanec, Z, Cejka, J. *Collection of Czechoslovak Chemical Communications* 1974**; 39**: 2891.
5. Urbanec, Z, Cejka, J. *Collection of Czechoslovak Chemical Communications* 1979**; 44**: 10.
6. Urbanec, Z, Cejka, J. *Collection of Czechoslovak Chemical Communications* 1979**; 44**: 1.
7. Cejka, J, Urbanec, Z. *Collection of Czechoslovak Chemical Communications* 1973**; 38**: 2327.
8. Christ, CL, Clark, JR, Evans, HT, Jr. *Science (Washington, DC, United States)* 1955**; 121**: 472.
9. Clark, JR, Christ, CL. *Am. Mineralogist* 1956**; 41**: 844.
10. Vochten, R, Deliens, M. *Canadian Mineralogist* 1998**; 36**: 1077.
11. Cejka, J, Mrazek, Z, Urbanec, Z. *Neues Jahrbuch fuer Mineralogie, Monatshefte* 1984: 109.
12. Melon, J. *Bull. inst. roy. colon. belge* 1938**; 9**: 333.
13. Baran, V, Skvor, F, Vosecek, V. *Inorganica Chimica Acta* 1984**; 81**: 83.
14. Anderson, A, Chieh, C, Irish, DE, Tong, JPK. *Canadian Journal of Chemistry* 1980**; 58**: 1651.
15. Cejka, J, Urbanec, Z, Cejka, J, Jr. *Neues Jahrbuch fuer Mineralogie, Monatshefte* 1987: 488.
16. Cejka, J, Urbanec, Z. *Journal of Thermal Analysis* 1988**; 33**: 389.
17. Elton, NJ, Hooper, JJ. *Mineralogical Magazine* 1992**; 56**: 124.
18. Meyrowitz, R, Ross, DR. *U.S. Geological Survey Professional Paper* 1961**; No. 424-B**: 266.
19. Cejka, J. *Collection of Czechoslovak Chemical Communications* 1969**; 34**: 1635.
20. Burns, PC. *Canadian Mineralogist* 2005**; 43**: 1839.
21. Burns, PC. *Reviews in Mineralogy* 1999**; 38**: 23.
22. Frost, RL, Henry, DA, Erickson, K. *Journal of Raman Spectroscopy* 2004**; 35**: 255.
23. Frost, RL, Carmody, O, Erickson, KL, Weier, ML, Cejka, J. *Journal of Molecular Structure* 2004**; 703**: 47.
24. Frost, RL, Erickson, KL, Weier, ML, Carmody, O, Cejka, J. *Journal of Molecular Structure* 2005**; 737**: 173.
25. Frost, RL, Weier, ML, Cejka, J, Ayoko, GA. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* 2006**; 65**: 529.
26. Frost, RL, Erickson, KL, Cejka, J, Reddy, BJ. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* 2005**; 61**: 2702.
27. Frost, RL, Weier, ML, Bostrom, T, Cejka, J, Martens, W. *Neues Jahrbuch fuer Mineralogie, Abhandlungen* 2005**; 181**: 271.
28. Frost, RL, Carmody, O, Erickson, KL, Weier, ML, Henry, DO, Cejka, J. *Journal of Molecular Structure* 2004**; 733**: 203.

29. Frost, RL, Weier, ML, Ayoko, GA, Martens, W, Cejka, J. *Mineralogical Magazine* 2006**; 70**: 299.
30. Urbanec, Z, Cejka, J. *Casopis Narodniho Muzea v Praze, Rada Prirodovedna* 1979**; 148**: 16.
31. Omori, K, Kerr, PF. *Geological Society of America Bulletin* 1963**; 74**: 709.
32. Ondrus, P, Skala, R, Veselovsky, F, Sejkora, J, Vitti, C. *American Mineralogist* 2003**; 88**: 686.
33. Paulis, P, Sikola, D, Holeczy, D. *Vestnik Ceskeho Geologickeho Ustavu* 1994**; 69**: 87.
34. Frondel, C. *U.S. Geological Survey Bulletin* 1958**; No. 1064**: 400 pp.
35. Jones, GC, Jackson, B *Infrared transmission spectra of carbonate minerals*; Chapman and Hall: London, 1993.
36. Mereiter, K. *TMPM, Tschermaks Mineralogische und Petrographische Mitteilungen* 1986**; 35**: 1.
37. Frost, RL, Bouzaid, JM, Martens, WN, Reddy, BJ. *Journal of Raman Spectroscopy* 2007**; 38**: 135.
38. Frost, RL, Cejka, J, Weier, ML. *Journal of Raman Spectroscopy* 2007**; 38**: 460.
39. Frost, RL, Cejka, J, Weier, ML, Martens, WN, Ayoko, GA. *Journal of Raman Spectroscopy* 2007**; 38**: 398.
40. Frost, RL, Palmer, SJ, Bouzaid, JM, Reddy, BJ. *Journal of Raman Spectroscopy* 2007**; 38**: 68.
41. Frost, RL, Weier, ML, Williams, PA, Leverett, P, Kloprogge, JT. *Journal of Raman Spectroscopy* 2007**; 38**: 574.
42. Frost, RL. *Journal of Raman Spectroscopy* 2006**; 37**: 910.
43. Frost, RL, Cejka, J, Weier, M, Ayoko, GA. *Journal of Raman Spectroscopy* 2006**; 37**: 1362.
44. Frost, RL, Cejka, J, Weier, M, Martens, WN. *Journal of Raman Spectroscopy* 2006**; 37**: 879.
45. Frost, RL, Henry, DA, Weier, ML, Martens, W. *Journal of Raman Spectroscopy* 2006**; 37**: 722.
46. Frost, RL, Weier, ML, Cejka, J, Kloprogge, JT. *Journal of Raman Spectroscopy* 2006**; 37**: 585.
47. Frost, RL, Weier, ML, Reddy, BJ, Cejka, J. *Journal of Raman Spectroscopy* 2006**; 37**: 816.
48. Frost, RL, Weier, ML, Martens, WN, Kloprogge, JT, Kristof, J. *Journal of Raman Spectroscopy* 2005**; 36**: 797.
49. Frost, RL, Kloprogge, JT, Martens, WN. *Journal of Raman Spectroscopy* 2004**; 35**: 28.
50. Frost, RL, Weier, ML. *Journal of Raman Spectroscopy* 2004**; 35**: 299.
51. Frost, RL, Musumeci, AW, Kloprogge, JT, Adebajo, MO, Martens, WN. *Journal of Raman Spectroscopy* 2006**; 37**: 733.
52. Frost, RL, Cejka, J, Weier, ML, Martens, W. *Journal of Raman Spectroscopy* 2006**; 37**: 538.
53. Frost, RL, Wills, R-A, Weier, ML, Martens, W. *Journal of Raman Spectroscopy* 2005**; 36**: 435.
54. Fan, H, Tao, K, Xie, Y, Wang, K. *Yanshi Xuebao* 2003**; 19**: 169.
55. Hong, W, He, S, Huang, S, Wang, Y, Hou, H, Zhu, X. *Guangpuxue Yu Guangpu Fenxi* 1999**; 19**: 546.

56. Anthony, JW, Bideaux, RA, Bladh, KW, Nichols, MC *Handbook of Mineralogy*; Mineral Data Publishing: Tiscon, Arizona, USA, 2003; Vol. 5.
57. Frost, RL. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* 2004**; 60A**: 1469.
58. Frost, RL, Kloprogge, JT. *Neues Jahrb. Mineral., Monatsh.* 2001: 27.
59. Martens, W, Frost, RL, Kloprogge, JT, Williams, PA. *Journal of Raman Spectroscopy* 2003**; 34**: 145.
60. Urbanec, Z, Cejka, J. *Therm. Anal., [Proc. Int. Conf. Therm. Anal.], 6th* 1980**; 2**: 359.
61. Cejka, J, Sejkora, J, Mrazek, Z, Urbanec, Z, Jarchovsky, T. *Neues Jahrbuch fuer Mineralogie, Abhandlungen* 1996**; 170**: 155.
62. Cejka, J. *Reviews in mineralogy* 1999**; 38**.
63. Cejka, J. *Reviews in Mineralogy* 1999**; 38**: 521.
64. Bartlett, JR, Cooney, RP. *J. Mol. Structure* 1989**; 193**: 295.
65. Farmer, VC *Mineralogical Society Monograph 4: The Infrared Spectra of Minerals*, 1974.
66. Cejka, J, Urbanec, Z, Cejka, J, Jr., Mrazek, Z. *Neues Jahrbuch fuer Mineralogie, Abhandlungen* 1988**; 159**: 297.
67. Libowitzky, E. *Monatshefte für Chemie* 1999**; 130**: 1047.

List of Figures


Schrockingerite
NaCa3(UO2)(CO3)(SO4)F.10H2O
Wyoming
815
1092
983
742
157
1374
707
308
471
Raman Intensity
1500
1300
1100
900
700
500
300
100
Wavenumber/cm-1

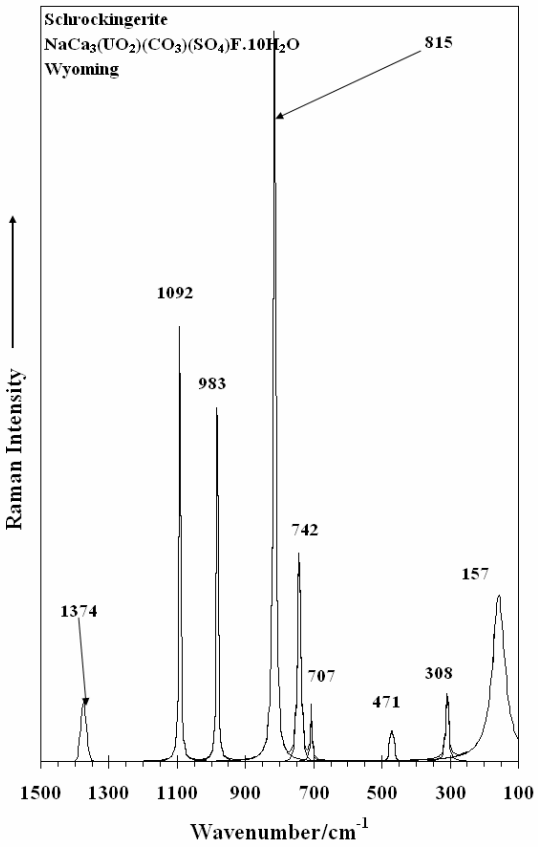

Schrockingerite
NaCa3(UO2)(CO3)(SO4)F.10H2O
Wyoming
815
1092
983
742
157
1374
707
308
471
Raman Intensity
1500
1300
1100
900
700
500
300
100
Wavenumber/cm-1

Figure 1

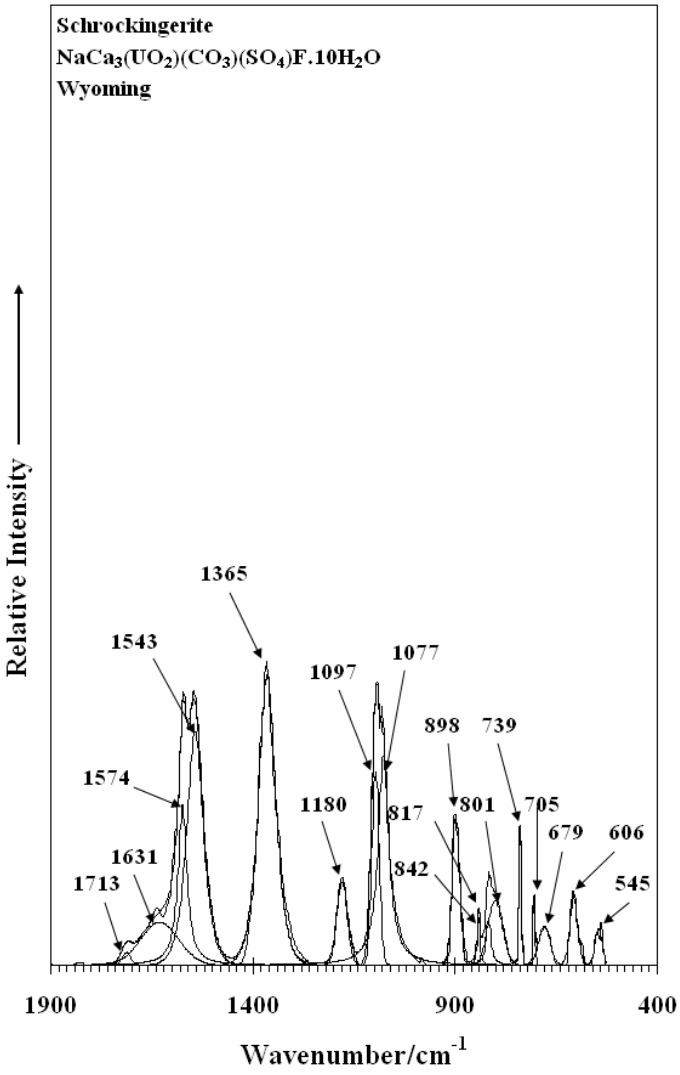

Schrockingerite
NaCa3(UO2)(CO3)(SO4)F.10H2O
Wyoming
Relative Intensity
1365
1543
1097
1077
898
739
1574
1180
817
801
705
679
606
1631
1713
842
545
1900
1400
900
400
Wavenumber/cm-1

Figure 2

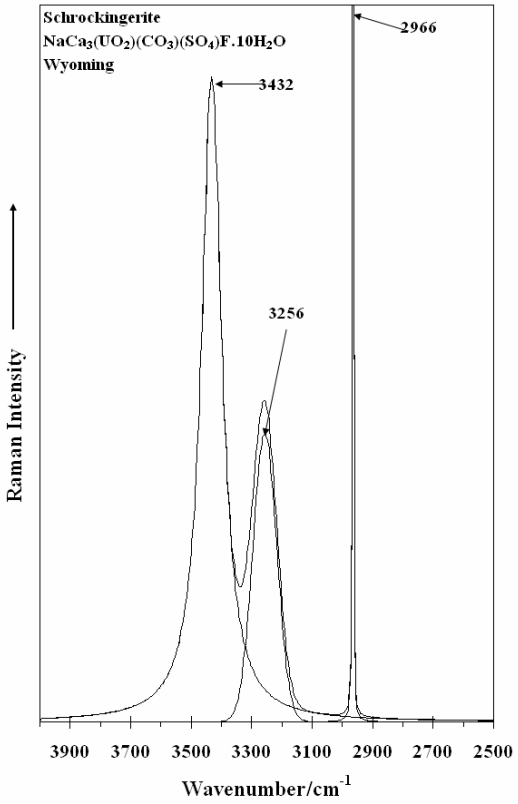

Schrockingerite
NaCa3(UO2)(CO3)(SO4)F.10H2O
Wyoming
3432
2966
3256
Raman Intensity
3900 3700 3500 3300 3100 2900 2700 2500
Wavenumber/cm-1

Figure 3

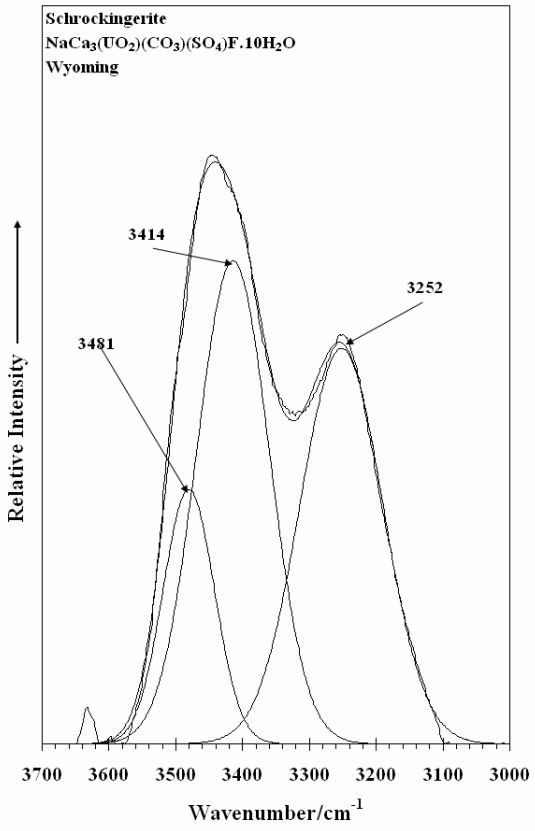

Schrockingerite
NaCa3(UO2)(CO3)(SO4)F.10H2O
Wyoming
3414
3252
3481
Relative Intensity
3700
3600
3500
3400
3300
3200
3100
3000
Wavenumber/cm-1

Figure 4